

REMARKS

Rejection under 35 USC §112(1)

Claim 1 is rejected under 35 USC §112(1) in that the amendments made to disclaim the compounds disclosed by Baird, *Tetrahedron Letters*, Vol. 36, No. 52, pp. 9541-9542 (1995) are considered new matter and are a negative limitation to the claim.

The amendments to Claim 1 made in the response dated October 13, 2009 have made this rejection moot in that the compounds disclosed in Baird are no longer included in the scope of the claims. The amendments did not introduce new matter in that the amendments were fully supported in the Specification as one of the preferred embodiments. The amendment to Claim 1 paragraph a) provides that only one of the substituent groups on the cyclopropene ring is other than hydrogen. This amendment is fully supported in the specification, page 6, lines 17-18. The compounds disclosed by Baird all have at least two non-hydrogen groups on the cyclopropene ring. Therefore, this amendment neither introduces new matter nor is it a negative limitation in the claim. Applicants, therefore, respectfully request that this rejection be withdrawn.

Rejection under 35 USC §112, First Paragraph Scope of Enablement

Claim 1 is rejected under 35 USC §112, First Paragraph, in that the Specification does not reasonably provide enablement for all the compounds as claimed. The factors to be considered in determining whether a disclosure meets the enablement requirement are those of *In re Wands*, 8 USPQ2nd 1400 (Fed. Cir. 1988) specifically: The nature of the invention; The predictability or unpredictability of the art; The breadth of the claims; The amount of direction of guidance presented; The presence or absence of working examples; and The quantity of experimentation necessary.

Applicants have included sufficient examples of preparation of the claimed compounds that one skilled in the organic synthesis art would be able to prepare any one of the claimed compounds without undue experimentation. The Specification provides specific detailed synthesis examples of cyclopropenes monosubstituted with a "G" containing group (see compounds numbered 1-5, 9, 10, 12-15, 36, 44, 47, 53, 55-59). In addition, the Specification provides detailed synthesis examples of other cyclopropenes substituted with a "G" containing group (see compounds 6-8, 11, 37-39, 41, 45, 46, 60) as well as descriptions of similar

compounds in Table 1. The exemplified compounds include a variety of both carbocyclic and heterocyclic "G" groups, wherein the heterocycle contains one or more oxygen, nitrogen, and sulfur.

Furthermore, Applicants contend that each of the *Wands* factors, in fact, have been met by the disclosure of the instant application. Specifically:

(1) The nature of the Invention - Although the presently claimed invention is drawn to cyclopropene compounds which contains a large Markush group of substituents, this group of substituents is, in fact, not as broad as it may first appear. All of the claimed compounds are monosubstituted and must include a substituent group that contains a carbocyclic or heterocyclic ring. This group of substituents provides cyclopropene compounds with ethylene inhibitory activity that were not previously disclosed in the art. Applicants are entitled to claim the full scope of those new compounds.

(2) Predictability - It is known within the art surrounding cyclopropene compounds that certain of them may have ethylene inhibition activity when contacted with plants or plant products. Many of these effects are documented in the references cited in applicant's Information Disclosure Statements. What was not known from those prior disclosures was the breadth of substituent groups which would provide the cyclopropene compounds with this activity. Applicants have discovered that the scope of active compounds goes far beyond those disclosed in the cited references. Applicants are not relying on a single, or a few, species in which to base the breadth of their claims. Rather, Applicants have shown through the eighty-six example compounds tested (fifty-six of which now fall within the scope of the amended claim) that a wide variety of compounds with widely varying substituents are active. These example compounds support the fact that within classes of substituent groups one skilled in the art can predict that certain compounds which are members of those classes will be active. In addition, Applicants have provided detailed synthesis examples for twenty claimed compounds and detailed synthesis examples for eleven similar compounds as well as descriptions of general synthetic methods which are applicable to preparation of the claimed compounds (see the Specification, page 12, line 26 to page 16, line 2 and the Examples, page 16 to page 64). One skilled in the art of synthetic organic chemistry would be able to predict which synthesis methods would be appropriate to prepare any one of the claimed compounds, without undue experimentation.

Applicants are not required to present any examples at all, and the C.C.P.A. has stated that the claims may be supported "either by the use of illustrative examples or by broad terminology." *In re Marzocchi*, 439 F.2d at 223 (C.C.P.A. 1971). Applicants respectfully submit that the teachings of their application provide the required support for the claims.

(3) Breadth of Claims - Admittedly, the claims of the instant application are broad. However, Applicants have provided a large number of example compounds (eighty-six, fifty-six of which fall within the scope of the amended claims) which: "...differ radically in their properties..." and which are demonstrated in the test results in the Specification, Table 3, pp 70-72 to "accomplish the desired result." These results amply demonstrate that the compounds included in the claims can be synthesized and are capable of accomplishing the desired results.

(4) Amount of Direction or Guidance Presented - The Office Action in states that there is no guidance or direction presented to enable one skilled in the art to make any one of the thousands of cyclopropene compounds as claimed. As noted above, there are fifty-six working examples of synthesized compounds and an additional thirty which are described. Extensive methods of synthesis are provided in the Specification, page 12, line 26 to page 16, line 2 and in the Examples, page 16 to page 64. With the information provided, one skilled in the art of organic synthesis would be able to develop specific methods to synthesize any one of the claimed compounds without undue experimentation. One skilled in the art of organic synthesis would also be well schooled in obtaining, or synthesizing, required starting materials to utilize in the cyclopropene syntheses. All of this can be accomplished without undue experimentation on the part of the chemist.

(5) Presence or Absence of Working Examples - The Office Action states that there are no examples presented to enable one skilled in the art to make any one of the thousands of cyclopropene compounds as claimed. Again, as noted above, there are presented in the specification a reasonable number of working examples and references to a large number of synthesis methods. The working examples include a large number of substituent groups which contain heterocyclic ring groups, each of which show the desired biological activity. These are sufficient to enable one skilled in the art to synthesize the claimed compounds with the expectation that they will provide the desired biological activity.

(6) The Quantity of Experimentation Necessary - The Office Action states that there is no guidance and/or direction provided by the Applicants for the wide variety of compounds and their preparation and method of use. However, as noted above, eighty-six example compounds are provided with the results of their use. Applicants are now only claiming a limited class of those compounds, those with only a single substituent group containing a "G" group. These data are presented in the synthesis examples (Specification, page 12, line 26 to page 16, line 2 and in the Examples, page 16 to page 64, and the test data presented on pp 69-72). The Office Action does not present facts to support the assertion that "undue experimentation" would be required to practice the present invention. Rejection of claims as being non-enabled requires "the Patent Office, whenever a rejection on this basis is made, to explain why it doubts the truth or accuracy of any statement in a supporting disclosure and to back up assertions of its own with acceptable evidence or reasoning" refuting the asserted teaching of the invention. *In re Marzocchi*, 439 F.2d 220, 224 (C.C.P.A. 1971). The Office has not met its burden to provide such evidence or reasoning. "However, specific technical reasons are always required." M.P.E.P. § 2164.04. The rejection merely states that there are not "sufficient working examples" to support the claims. Applicants are not required to present any examples at all, and the C.C.P.A. has stated that the claims may be supported "either by the use of illustrative examples or by broad terminology." *In re Marzocchi*, 439 F.2d at 223. Applicants respectfully submit that the broad teachings of their application, the broadly described synthesis methods, and the extensive synthesis examples provide the required support for the claims. The mere assertion that there is not "a sufficient number of compounds to support the relatively broad claims" has been rejected previously by the Board of Patent Appeals and Interferences, which reversed such an enablement rejection as "not supported by evidence, facts or sound scientific reasoning." *Ex parte Reese*, 40 U.S.P.Q.2d 1221 (B.P.A.I. 1996).

Applicants, respectfully request that this rejection be withdrawn.

Rejection under 35 USC §103(a)

Claim 1 is rejected under 35 USC §103(a) as being unpatentable over Sisler, E. (US 6,194,350 and 6,365,549), Daly, et.al. (US 6,017,849), and Minkin, et.al. *Journal of Molecular Structure*, 398-399 (1997) pp. 237-253 in that each of the references teaches cyclopropene derivatives and methods of blocking ethylene receptors in plants.

The Office Action is correct in that in the broadest sense, each of the cited references teaches cyclopropene derivatives. However, only Sisler and Daly teach methods of blocking the ethylene response in plants. Even though Sisler teaches extensive substitution on the cyclopropene ring, those substitutents are, in fact, quite limited in scope. Sisler teaches that the substituent groups are linear or branched chain...C₆ - C₂₀ alkyl, alkenyl, or alkynyl...and may include compounds in which one or more of the carbons is replaced by heteroatoms...or where such chains include halogen, amino, alkoxy, carboxy, alkoxycarbonyl, or hydroxy substituents. Daly teaches similar substituents to those taught by Sisler, except that Daly's substituent groups are much smaller and even more limited in scope (i.e. C₁ - C₄ alkyl, hydroxy, halogen, C₁ - C₄ alkoxy, amino, and carboxy, See Daly, col. 6, lines 30-32). Neither Sisler nor Daly, either alone or in combination, teach, disclose, or suggest substituents which contain Applicants' carbocyclic or heterocyclic ring systems. In fact, the disclosures of Sisler and Daly teach away from substituents containing complex groups. Both Sisler and Daly specifically teach that linear chains are preferred (see Sisler, col. 2, lines 45-46 "Alkyl groups of the present invention are preferably linear and saturated." and Daly, col. 6, lines 37-41 "The preferred compounds capable of inhibiting the ethylene response in plants ...are cyclopropene and dimethylcyclopropene."). Thus, Sisler and Daly, in combination, direct one skilled in the art away from Applicants' carbocyclic and heterocyclic rings and toward linear and saturated substituent groups.

Minkin presents a completely different problem and solution from those addressed by Sisler and Daly. Sisler and Daly relate to the use of cyclopropenes to inhibit the ethylene response in plants while Minkin relates to computational modeling of the mechanisms of circumambulatory rearrangements of main-group migrants (that is, substituents) in the cyclopropene ring. There is no disclosure, teaching, or suggestion of biological activity of any kind in Minkin. Minkin is concerned with the various mechanistic factors related to substituent group migrations in the cyclopropene ring and comparison of those factors with substituent group migrations in cyclopentadienes (see the Abstract; page 238, first full paragraph; page 251, Conclusions). In addition, Minkin does not actually disclose the synthesis of any compound discussed. Rather, the reference is limited to computational modeling of hypothetical compounds (see the Abstract; page 238, first column, line 22 to end of paragraph; page 238, Methods; page 239 first column, lines 8-11; page 243, first column, lines 18-21; page 247 first

column, lines 4-7 and second column). Therefore, Minkin should not be considered as being an enabling reference as it does not describe the synthesis of any particular cyclopropene nor their use for any purpose other than computational, mechanistic studies. It is still Applicants' position that Minkin is not a valid reference for obviousness, either alone or in combination with '350, '549, and/or '849. Minkin does disclose a theoretical cyclopropene substituted with a phenylthio group. Again, however, one skilled in the art, with knowledge of Minkin, Sisler, and Daly, would not be directed to the synthesis of cyclopropenes containing carbocyclic and/or heterocyclic rings in light of the preferences in Sisler and Daly which specifically prefer linear, saturated substituents.

One skilled in the art would conclude, therefore, that there is no disclosure, teaching, or suggestion in Sisler, Daly, or Minkin, either alone or in combination, that would motivate such a person to synthesize cyclopropenes substituted with substituent groups containing carbocyclic and/or heterocyclic rings with the expectation that such compounds would provide inhibition of the ethylene response in plants. Applicants, therefore, respectfully request that this rejection be withdrawn

Provisos in the Claim

The Examiner has requested information regarding the prior art which has been disclaimed by the proviso. The disclaimed references the following: Minkin (described above); Ryu, et.al., *J. American Chemical Society*, 1990, 112(19), pp. 7061-7063 (provided in Supplemental Information Disclosure in the May 6, 2008 response to a prior Official Action) and Karnienska-Trela, et. al., *Magnetic Resonance in Chemistry* (2002), 40(10), 640-646 (trimethylsilyl); Gosse, et. al., *Canadian Journal of Chemistry* (2004), 82(11), 1589-1596 (thiol); Yet, L., *Dissertation Abstract Int.*, B 1995, 6(6), 3208 (phenylsulfonyl); Weber, et.al., *Helvetica Chimica Acta* (1989), 72(1), 29-40 (phenylthioethyl); Malek, J., *Organic Reactions* (Hoboken, NJ, United States (1988), 36 (diphenylhydroxymethyl); Albertson, et.al., US 3,898,235 (benzo[g]quinolin-7-ol-1-methyl); and Paredes, et.al., *Revista Latinoamericana de Quimica* (1985), 16(2-3), 94-8 (malonates). These references were not considered material to patentability by the inventors in that they disclose reaction pathway studies, physico-chemical studies, or compounds used for purposes much different than the uses envisioned by the inventors for their

claimed compounds. Copies of abstracts of the non-patent references are attached to this response.

Rejection under 35 USC §103(a) - Second Rejection

Claim 1 is rejected under 35 USC §103(a) over Baird, et.al., *Tetrahedron Letters*, Vol. 36, No. 52, pp. 9541-9542 (1995) in that Baird teaches an unusual rearrangement of 1-allyl and 1-benzylcyclopropenes.

Baird is much like Minkin (see above) in that Baird is directed toward studies of rearrangements in certain specifically substituted cyclopropene rings (i.e. allyl and benzyl substituents). The purpose of Baird's studies is to provide a method to protect the strained cyclopropene ring (see p. 9541, first paragraph) and as a possible applicable route to prepare 1,2-disubstituted bicyclo[1.1.0]butanes (see p. 9542, end of last paragraph). There is no disclosure, teaching, or suggestion in Baird that would motivate one of ordinary skill in the art to prepare allyl and/or benzyl substituted cyclopropenes with the expectation of obtaining a compound that would inhibit the effect of ethylene on plants. There is no disclosure, teaching, or suggestion in Baird of any biological activity of any kind with respect to the compounds disclosed. Applicants, therefore, respectfully request that this rejection be withdrawn.

Conclusion regarding 35 USC §103(a) rejections

There is no disclosure, teaching, or suggestion in any one of the cited references (Sisler, Daly, Minkin, and Baird) either alone or in combination, that would make the subject matter defined by the instant claims obvious to one skilled in the art of organic synthesis and ethylene response inhibition in plants. Sisler and Daly both disclose certain cyclopropenes with limited substituent groups, which are inhibitors of the ethylene response in plants. However, neither disclose cyclopropenes in which the substituent groups include a carbocyclic or heterocyclic ring. In fact, each of Sisler and Daly teach that short chains that are linear and saturated are preferred. This would suggest to one skilled in the art that substituent groups with carbocyclic or heterocyclic rings (both much larger than corresponding alkyl chains) would not exhibit the desired ethylene inhibition activity. Applicants' data clearly show that this is not the case. Minkin and Baird address a completely different problem than that addressed by Sisler and Daly. Both Minkin and Baird relate to studies of rearrangements of substituent groups around a

RECEIVED
CENTRAL FAX CENTER

MAY 19 2010

cyclopropene ring. There is no disclosure, teaching, or suggestion in either Minkin or Baird that any of the disclosed cyclopropenes would be useful as ethylene inhibitory compounds.

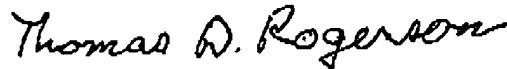
Rejection under 35 USC §102(b)

Claim 1 is rejected under 35 USC §102(b) as being anticipated by Baird (see above) which discloses 1-butyl-2-(3-methylbut-2-enyl)cyclopropene and 2-(4'-methoxybenzyl)-1-pentylcyclopropene.

As amended in the prior response, none of the compounds disclosed in Baird are included within the scope of Claim 1. Specifically, Claim 1 is now limited to monosubstituted cyclopropenes in which the substituent includes at least one carbocyclic or heterocyclic ring. Applicants, therefore, respectfully request that this rejection be withdrawn.

With this amendment and response, Applicants believe that the prior rejections have been overcome and the claims are in condition for allowance. Should the Examiner have any suggestions which may put the Application in better condition for allowance, Applicants' attorney is willing to discuss any such suggestions either by phone or at the U. S. Patent and Trademark Office.

Respectfully submitted,



Thomas D. Rogerson, Ph.D.
Attorney for Applicants
Registration No. 38,602
Telephone: 215-619-1569

Patent Department, 9th Floor
Rohm and Haas Company
100 Independence Mall West
Philadelphia, PA 19106-2399
Date: May 19, 2010

AP6187Attachment

10/645431

L4 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
 RN 151568-69-3 REGISTRY
 ED Entered STN: 03 Dec 1993
 CN Cyclopropene, 1-(trimethylsilyl)- (CA INDEX NAME)
 OTHER CA INDEX NAMES:
 CN Silane, 1-cyclopropen-1-yltrimethyl- (9CI)
 OTHER NAMES:
 CN 1-Trimethylsilylcyclopropene
 MF C6 H12 Si
 SR CA
 LC STN Files: CA, CAPLUS
 DT.CA CAplus document type: Journal
 RL.NP Roles from non-patents: PREP (Preparation); PRP (Properties)

 SiMe3

Kamienska-Trela

See HELP PROPERTIES for information about property data sources in REGISTRY.
 2 REFERENCES IN FILE CA (1907 TO DATE)
 2 REFERENCES IN FILE CAPLUS (1907 TO DATE)

REFERENCE 1

AN 138:153171 CA Full-text
 TI One-bond ^{13}C - ^{13}C coupling constants in alkyl-substituted cyclopropenes:
 experimental and theoretical studies
 AU Kamienska-Trela, Krystyna; Bernatowicz, Piotr; Luttko, Wolfgang; Machinek,
 Reinhard; Traetteberg, Marit
 CS Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw,
 01-224, Pol.
 SO Magnetic Resonance in Chemistry (2002), 40(10), 640-646
 CODEN: MRCHEG; ISSN: 0749-1581
 PB John Wiley & Sons Ltd.
 DT Journal
 LA English
 CC 22-10 (Physical Organic Chemistry)
 AB Measurements of 1-bond C-C coupling consts., $^{1}\text{J}(\text{C},\text{C})$, were performed for two
 series of compds., alkyl-substituted cyclopropenes and cyclopropanes. The
 exptl. data were complemented by a set of DFT-calculated J couplings for the
 parent cyclopropene (1), its Me and silyl derivs. and, addnl., for 1-
 methylcyclobutene (3), 1-methylcyclopentene (4) and 1-methylcyclohexene (5)
 and good agreement was observed between the exptl. and the calculated data;
 all the trends are perfectly maintained, including a dramatic decrease in the
 couplings across endocyclic single bonds in cyclopropene and its derivs., and
 a significant decrease in the corresponding couplings in cyclobutene. Using
 the data obtained, the s characters of the C hybrid orbitals involved in the
 formation of the cyclopropene were calculated. The ring closure and the
 related strain exerted upon the cyclopropene mol. only slightly disturb the

9/22/2009
 Page 2 /

MAY 19 2010

electron structure of the double bond. The s character of the corresponding C orbital is 0.314 in cyclopropene vs. the theor. value of 0.333 in ethene. This is at variance with the endo- and exocyclic single bonds, where the s characters of the orbitals forming the endocyclic single bonds are much smaller than those of the bonds in the open-chain compds., i.e. 0.229 (C-1 and/or C-2) and 0.166 (C-3). The s values calculated for the exocyclic CH bonds are 0.334 for C-3 and 0.456 for C-1 and/or C-2.

ST one bond carbon coupling alkylcyclopropene theor exptl

IT Density functional theory

Perturbation theory
(SOS_DFPT; exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

IT Double bond
(carbon-carbon, effect of mol. strain and cyclization on electronic structure; exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

IT Electronic structure
(double bond; exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

IT Strain
(effect of mol. strain on double bond electronic structure; exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

IT Cyclization
(effect on double bond electronic structure; exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

IT Nuclear spin-spin coupling
(1JCC; exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

IT 74-85-1, Ethene, properties 75-19-4, Cyclopropane 115-07-1, 1-Propene, properties 513-35-9 591-49-1, 1-Methylcyclohexene 594-11-6 627-20-3 646-04-8 693-89-0, 1-Methylcyclopentene 754-05-2 1453-25-4, 1-Methylcycloheptene 1489-60-7, 1-Methylcyclobutene 1630-94-0 3100-04-7, 1-Methylcyclopropene 3664-56-0 3907-06-0 4127-45-1 51314-28-4 80816-10-0 126361-33-9 140421-96-1 148312-18-9 151568-69-3

RL: PRP (Properties)
(exptl. and theor. studies of one-bond ^{13}C - ^{13}C coupling consts. in alkyl-substituted cyclopropenes)

RE.CNT 39 THERE ARE 39 CITED REFERENCES AVAILABLE FOR THIS RECORD

- (1) Ahlrichs, R; Chem Phys Lett 1989, V162, P165 CAPLUS
- (2) Barszczewicz, A; Theor Chim Acta 1993, V87, P19 CAPLUS
- (3) Becke, A; J Chem Phys 1988, V88, P1053 CAPLUS
- (4) Becke, A; Phys Rev A 1988, V38, P3098 CAPLUS
- (5) Contreras, R; Ann Rep NMR Spectrosc 2000, V41, P57
- (6) Eckert-Maksic, M; J Mol Struct (THEOCHEM) 1982, V86, P325
- (7) Finkelman, H; J Am Chem Soc 1978, V100, P6262
- (8) Fitjer, L; Chem Ber 1986, V119, P1144 CAPLUS
- (9) Foerster, T; Z Phys Chem B 1939, V43, P58
- (10) Frish, M; Gaussian 94 Rev B1 1995
- (11) Fronzoni, G; J Magn Reson 1987, V71, P229 CAPLUS
- (12) Guenther, H; Chem Ber 1973, V106, P3938 CAPLUS
- (13) Guenther, H; Org Magn Reson 1976, V8, P299 CAPLUS
- (14) Haeser, M; Theor Chim Acta 1992, V83, P455 CAPLUS
- (15) Jankowski, P; J Organomet Chem 1993, V460, P15 CAPLUS
- (16) Kalinowski, H; Carbon-13 NMR Spectroscopy 1994
- (17) Kamienska-Trela, K; Annu Rep NMR Spectrosc 1995, V30, P131 CAPLUS

9/22/2009
Page 31

L13 ANSWER 1 OF 2 REGISTRY COPYRIGHT 2009 ACS on STN
 RN 81788-91-2 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN 2-Cyclopropene-1-thiol (CA INDEX NAME)
 MF C3 H4 S
 LC STN Files: CA, CAPLUS
 DT.CA CAplus document type: Journal
 RL.NP Roles from non-patents: PROC (Process); PRP (Properties); RACT
 (Reactant or reagent)

SH

Gosse

See HELP PROPERTIES for information about property data sources in REGISTRY.
 4 REFERENCES IN FILE CA (1907 TO DATE)
 4 REFERENCES IN FILE CAPLUS (1907 TO DATE)

REFERENCE 1

AN 142:391925 CA Full-text
 TI Exo selectivity and the effect of disubstitution in the Diels-Alder reactions of butadiene with 3,3-disubstituted cyclopropenes
 AU Gosse, Tammy L.; Poirier, Raymond A.
 CS Department of Chemistry, Memorial University of Newfoundland, St. John's, NL, A1B 3X7, Can.
 SO Canadian Journal of Chemistry (2004), 82(11), 1589-1596
 CODEN: CJCHAG; ISSN: 0008-4042
 PB National Research Council of Canada
 DT Journal
 LA English
 CC 22-2 (Physical Organic Chemistry)
 AB A d. functional computational study was performed to accomplish two tasks: to examine the endo-exo selectivity in the Diels-Alder reactions of 3,3-disubstituted cyclopropenes with s-cis-butadiene, and to study the effect of disubstitution on the reactivity of the cyclopropene dienophile. Cyclopropene is substituted at C-3 with CH₃, SiH₃, NH₂, PH₂, OH, SH, F, and Cl; both 3-substituted and 3,3-disubstituted ground states are examined to determine relative reactivities. The exo transition-state structures are consistently lower in energy than the endo transition-state structures for the 3,3-disubstituted cyclopropene - butadiene system, and surprisingly, both modes of addition have lower activation barriers than the syn 3-substituted cyclopropene - butadiene system. Through a series of isodesmic reactions, we have concluded that there is an addnl. stabilization in the transition-state structures of the 3,3-disubstituted system that can account for the lowering of the activation barriers below that of the 3-substituted cases. This stabilization is a combination of the anomeric effect and the ring relaxation that occurs in the transition-state structure.
 ST ab initio Diels Alder cycloaddn butadiene disubstituted cyclopropenes

9/22/2009
 Page 3

L17 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
 RN 174008-19-6 REGISTRY
 ED Entered STN: 08 Mar 1996
 CN Benzene, (1-cyclopropen-1-ylsulfonyl)- (CA INDEX NAME)
 OTHER NAMES:
 CN 1-(Benzenesulfonyl)cyclopropene
 MF C9 H8 O2 S
 SR CA
 LC STN Files: CA, CAPLUS
 DT.CA CAPLUS document type: Dissertation
 RLD.NP Roles for non-specific derivatives from non-patents: PREP (Preparation)

See HELP PROPERTIES for information about property data sources in REGISTRY.

- 1 REFERENCES IN FILE CA (1907 TO DATE)
- 1 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
- 1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

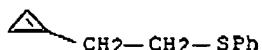
REFERENCE 1

yet

AN 124:175518 CA Full-text
 TI Chapter I. Synthesis and chemistry of
 1-(benzenesulfonyl)-2-(trimethylsilyl)cyclopropane. Chapter II.
 1,1-(Dilithio)-1-(benzenesulfonyl)-2-(trimethylsilyl)ethane as an
 effective synthetic equivalent for symmetrical 1,1-disubstituted terminal
 olefins.
 AU Yet, Larry
 CS Ohio State University, Columbus, OH, USA
 SO (1995) 144 pp. Avail.: University Microfilms Int., Order Number DA9534096
 From: Diss. Abstract Int., B 1995, 56(6), 3208
 DT Dissertation
 LA English
 CC 25-12 (Benzene, Its Derivatives, and Condensed Benzenoid Compounds)
 Section cross-reference(s): 24
 AB Unavailable
 ST benzenesulfonyltrimethylsilylcyclopropane; cyclopropane
 benzenesulfonyltrimethylsilyl; dilithiobenzenesulfonyltrimethylsilylethane
 synthon disubstituted terminal olefin; cyclopropene prepn synthon
 benzenesulfonyltrimethylsilylcyclopropane
 IT Synthons
 (preparation of (dilithio)(benzenesulfonyl)(trimethylsilyl)ethane as
 synthon
 for sym. 1,1-disubstituted terminal olefins)
 IT Alkenes, preparation
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (terminal: preparation of (dilithio)(benzenesulfonyl)(trimethylsilyl)ethane
 as synthon for sym. 1,1-disubstituted terminal olefins)
 IT 16984-48-8, Fluoride ion, reactions
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (eliminating reagent; preparation and chemical of
 (benzenesulfonyl)(trimethylsilyl)cyclopropane)
 IT 174008-13-0P, 1-(Benzenesulfonyl)-2-(trimethylsilyl)cyclopropane
 174008-15-2P, cis-1-(Benzenesulfonyl)-2-(trimethylsilyl)cyclopropane
 174008-16-3P, trans-1-(Benzenesulfonyl)-2-(trimethylsilyl)cyclopropane
 174008-17-4P, 1-(Benzenesulfonyl)-1-bromo-2-(trimethylsilyl)cyclopropane
 174008-18-5P, 1-(Benzenesulfonyl)-1-(trifluoromethanesulfonyl)-2-

9/22/2009
 Page 184

L20 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
 RN 121362-75-2 REGISTRY
 ED Entered STN: 30 Jun 1989
 CN Benzene, [(2-(1-cyclopropen-1-yl)ethyl)thio]- (CA INDEX NAME)
 MF C11 H12 S
 SR CA
 LC STN Files: CA, CAPLUS, CASREACT
 DT.CA CAplus document type: Journal
 RL.NP Roles from non-patents: PREP (Preparation)



See HELP PROPERTIES for information about property data sources in REGISTRY.
 1 REFERENCES IN FILE CA (1907 TO DATE)
 1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

REFERENCE 1

AN 111:38911 CA Full-text
 TI Fulvene, fulvalenes. Part 55. Generation and trapping of triafulvene
 AU Weber, Andreas; Staempfli, Urs; Neuenschwander, Markus
 CS Inst. Organic Chemical, University Bern, Bern, Ch-3012, Switz.
 SO Helvetica Chimica Acta (1989), 72(1), 29-40
 CODEN: HCACAV; ISSN: 0018-019X
 DT Journal
 LA English
 CC 24-7 (Alicyclic Compounds)
 GI

Weber



AB

Substituted methylidenecyclopropanes I [R = SPh, S(O)Ph, SO₂Ph, S+MePh], being easily available from 1,1-dibromo-2-(phenylthio)cyclopropane, are attractive precursors of triafulvene (2-methylidene-1-cyclopropene (II)). Both the sulfoxide and the sulfone I [R = S(O)Ph] react with an excess of alkoxides (KOCMe₃ and NaOMe) to give I (R = OCMe₃, OMe) resp., while the sulfinyl group of I [R = S(O)Ph, SO₂Ph] may be replaced by the PhCH₂S substituent in the presence of PhCH₂SH-KOCMe₃. These reactions may be explained by assuming II as a reactive intermediate, although an alternative sequence including carbene intermediates is not completely ruled out. Deuterium labeling expts. do not

9/22/2009
 Page 285

} give conclusive evidence due to deuterium scrambling, but
 deprotonation/methylation sequences show that H-C(2) of I is the most acidic
 proton. Final evidence for II results from the reaction of I (R = S+MePh)
 with cyclopentadienide to produce the expected [4 + 2] cycloaddn. product III.

ST triafulvene prepns Diels Alder cyclopentadiene; methylidenecyclopropane
 phenylthio elimination; methylidenecyclopropene prepns Diels Alder
 cyclopentadiene; cyclopropene methylidene

IT 13640-71-6
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (cyclopropanation of, with bromoform and base)

IT 78656-83-4
 RL: RCT (Reactant); RACT (Reactant or reagent).
 (deprotonation and methylation of)

IT 78656-80-1
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (deprotonation-silylation and silylation-addition reactions of, with
 butyllithium and chlorotrimethylsilane)

IT 94923-10-1
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (elimination reactions of, methylidenecyclopropene from)

IT 121362-68-3
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (elimination, rearrangement, and cycloaddn. reactions of)

IT 4095-06-1P
 RL: RCT (Reactant); PREP (Preparation); RACT (Reactant or reagent)
 (generation and trapping reactions of)

IT 121362-74-1P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation and conversion of, to methylidene sulfoxide)

IT 121362-75-2P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation and cycloaddn. of, with cyclopentadiene)

IT 121362-71-8P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
 (Reactant or reagent)
 (preparation and deuterium exchange reaction of)

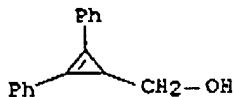
IT 121362-72-9P 121362-73-0P
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP (Preparation); RACT
 (Reactant or reagent)
 (preparation and epimerization of)

IT 19750-15-3P 23230-90-2P 78638-79-6P 78638-80-9P 78638-81-0P
 121362-69-4P 121362-70-7P 121362-76-3P 121362-77-4P
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (preparation of)

IT 4984-82-1, Sodium cyclopentadienide
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (reaction of, with methylidenecyclopropylsulfonium salt, cycloadduct
 from)

L29 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN
 RN 6415-73-2 REGISTRY
 ED Entered STN: 16 Nov 1984
 CN 2-Cyclopropene-1-methanol, 2,3-diphenyl- (CA INDEX NAME)
 OTHER NAMES:
 CN 2,3-Diphenyl-1-hydroxymethyl-2-cyclopropene
 MF C16 H14 O
 LC STN Files: BEILSTEIN*, CA, CAPLUS, CASREACT
 (*File contains numerically searchable property data)
 DT.CA CAplus document type: Journal
 RL.NP Roles from non-patents: FREP (Preparation); PRP (Properties); RACT
 (Reactant or reagent)

Ring System Data



Malek

See HELP PROPERTIES for information about property data sources in REGISTRY.
 11 REFERENCES IN FILE CA (1907 TO DATE)
 11 REFERENCES IN FILE CAPLUS (1907 TO DATE)

REFERENCE 1

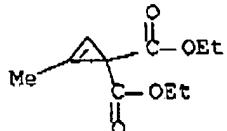
AN 149:555118 CA. Full-text
 TI Reductions by metal alkoxyaluminum hydrides. Part II. Carboxylic acids and derivatives, nitrogen compounds, and sulfur compounds
 AU Malek, Jaroslav
 CS Czech. Acad. Sci., Prague, Czech.
 SO Organic Reactions (Hoboken, NJ, United States) (1988), 36, No pp. given
 CODEN: ORHNBA
 URL: <http://www3.interscience.wiley.com/cgi-bin/mrwhome/107610747/HOME>
 PB John Wiley & Sons, Inc.
 DT Journal; General Review; (online computer file)
 LA English
 CC 21-0 (General Organic Chemistry)
 AB A review of the article Redns. by metal alkoxyaluminum hydrides. Part II. Carboxylic acids and derivs., nitrogen compds., and sulfur compds.
 ST review Carboxylic; review Alkoxyaluminum; review Redn; review Sulfur; review II; review Metal; review Acids; review Nitrogen; review Deriv; review Part; review Compd; review Hydrides
 IT Organic synthesis
 (Redns. by Metal Alkoxyaluminum Hydrides. Part II. Carboxylic Acids and Derivs., Nitrogen Compds., and Sulfur Compds.)
 IT 55-21-0, Benzamide 58-95-7 59-26-7 59-67-6, 3-Pyridinecarboxylic acid, reactions 62-23-7 65-85-0, Benzoic acid, reactions 67-64-1, 2-Propanone, reactions 69-72-7, reactions 70-47-3, L-Asparagine, reactions 74-11-3 78-82-0 79-03-8, Propanoyl chloride 79-09-4, Propanoic acid, reactions 79-20-9 79-30-1 79-46-9 80-62-6

9/22/2009
 Page 227

RECEIVED
CENTRAL FAX CENTER

MAY 19 2010

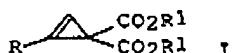
L37 ANSWER 2 OF 2 REGISTRY COPYRIGHT 2009 ACS on STN
 RN 106352-22-1 REGISTRY
 ED Entered STN: 31 Jan 1987
 CN 2-Cyclopropene-1,1-dicarboxylic acid, 2-methyl-, 1,1-diethyl ester
 (CA INDEX NAME)
 OTHER CA INDEX NAMES:
 CN 2-Cyclopropene-1,1-dicarboxylic acid, 2-methyl-, diethyl ester
 (9CI)
 MF C10 H14 O4
 SR CA
 LC STN Files: CA, CAPLUS
 DT CA CAplus document type: Journal
 RL.NP Roles from non-patents: PREP (Preparation)



See HELP PROPERTIES for information about property data sources in REGISTRY.
 1 REFERENCES IN FILE CA (1907 TO DATE)
 1 REFERENCES IN FILE CAPLUS (1907 TO DATE)

REFERENCE 1

AN 106:49630 CA Full-text
 TI Synthesis of cyclopropene-3,3-dicarboxylic esters
 AU Paredes, Rodrigo; Barba, Luz E.; Bastos, Holger; Garavito, Diego
 CS Dep. Quim., University Valle, Cali, 25360, Colombia
 SO Revista Latinoamericana de Quimica (1985), 16(2-3), 94-8
 CODEN: RLAQAB; ISSN: 0370-5943
 DT Journal
 LA English
 CC 24-2 (Alicyclic Compounds)
 GI



Paredes

AB Cyclopropenedicarboxylates I ($R = H, Me, Et, Ph; R_1 = Et, Me$) were prepared in up to 48% yield by treating $BrCH_2CR:C(CO_2R_1)_2$ with Me_3COK in Me_3COH or Me_2SO . Only a small amount of I ($R = H, R_1 = Et$) was obtained as $BrCH_2CH:C(CO_2Et)_2$ was unstable and easily polymerized.

ST cyclocondensation intramol bromoalkylenemalonate*

9/22/2009
 Page 388